Hydrogen

Introduction

This supplement addresses the hazards of hydrogen use and associated safety requirements at LLNL.

Hazards

Hydrogen possesses a number of unique properties which render it more hazardous than most other flammable gases. These hazards can be avoided through proper engineering and careful use. The hazards are:

Flammability

Hydrogen has an unusually large flammability range. It can form ignitable mixtures between 4% and 75% by volume in air. The range for explosive mixtures is also very broad. Given confinement and good mixing, hydrogen can be detonated over the range of 18% to 59% by volume in air.

Ignition

Hydrogen has an extremely low ignition energy requirement. A stoichiometric mixture can be ignited by a 20 μJ spark. (This is 10 times less than what is required to ignite a gasoline/air mixture.) Such sparks can be generated by most electrical equipment and by static charges on clothing or personnel. The auto-ignition temperature is 585°C.

Warning Properties

Hydrogen has no warning properties. It is a clear, colorless, odorless, and tasteless gas. It burns with an extremely hot but nonluminous flame. Hence, even the flame of burning hydrogen has few warning properties, and the extent of hydrogen fires is difficult to judge. These hazards are controlled by a combination of measures, including careful selection of location, limits on the amount of hydrogen available, good pressure-system engineering, control of ignition sources, and training of personnel.

Location of Hydrogen Systems

Hydrogen may be used only in well-ventilated laboratory areas. The amount of ventilation required will vary for each case, depending on the total supply of hydrogen, the use-rate, and venting arrangements from the hydrogen system. The Industrial Hygiene and/or Industrial Safety Groups can provide an evaluation in each case. As a general rule, most laboratories have sufficient ventilation to permit the use of some hydrogen without major modifications.

Hydrogen supplies should be located on the exteriors of buildings, and the gas should be piped to the laboratory at the lowest usable pressure. Manifolds and piping covered by Plant Engineering, Livermore (PEL) standards require no additional Engineering Safety Notes.

Avoid introducing hydrogen cylinders into buildings, even for temporary installations. Where this is unavoidable, locate the cylinder adjacent to a fume hood or in a ventilated cabinet. Common sense dictates the use of only the smallest possible cylinder in such a case. Always store extra cylinders outdoors.

Hydrogen System Design

All hydrogen systems with pressure greater than 150 psi, or with a volume greater than 2 liters and pressure greater than 75 psi, require Engineering Safety Notes. Refer to Health and Safety Manual Supplement 32.03 for details. In the design of hydrogen systems, give special attention to control of embrittlement, flammable mixtures, and ignition sources.

Embrittlement

Many metals undergo embrittlement upon exposure to hydrogen. Select suitable materials to safeguard against this. Austenitic stainless steels, monel, copper, and aluminum are generally satisfactory.

Flammable Mixtures

Confined hydrogen/air mixtures detonate instead of burn. The energy content per weight of a stoichiometric mixture of hydrogen and air is about the same as for TNT, although much less is converted into a pressure wave during the detonation. Hence, it is imperative to prevent the formation of flammable mixtures in the system. Make provisions for evacuating hydrogen systems or making them inert, both before and after use. For systems that are cycled frequently, give consideration to automatic inert-gas purge systems; for systems not normally exposed to air, it may be sufficient to provide simple purge connections.

Where air or other oxidizing gases connect to the same system as hydrogen, flash arrestors must be installed on both the hydrogen and oxidizer supply. No flash arrestor currently available is certified to work reliably with hydrogen under all conceivable circumstances. However, the flash arrestors available from Stores should function under most circumstances.

Ignition Sources

The system designer should take special care to assure that hydrogen is not exposed under normal or abnormal conditions to any ignition sources. For small systems this may require venting normal effluent and pressure-relief devices into a suitable exhaust duct; avoiding or carefully locating spark-producing motors and make-or-break electric contacts; or, placing the system in a fume hood or ventilated enclosure. For larger systems or in special applications it may be necessary to provide purged enclosures for potential ignition sources.

Safety Procedures

Any pressurized system using hydrogen must be authorized by a Safety Procedure. Routine use can be authorized in the Facility Safety Procedure (FSP). Unusual operations and those posing a substantial hazard should be covered by special Operational Safety Procedures (OSP). Use checklists for all but the simplest operations.

Hydrogen Alarms

Hydrogen alarms are required for systems with a large supply where a leak over an extended period of time could create an explosive mixture. Alarms are typically required in facilities serviced by tube trailer banks, for instance. Where alarms are required, a local evacuation alarm is sounded which is also forwarded to the Emergency Communications Center (Building 313). This allows the Fire Department to respond and shut off the supply to mitigate a potential disaster. Hydrogen alarms are not required for installations with fewer than 4 full-sized cylinders connected for use: a leak of sufficient size to create an explosion problem in such small systems would probably exhaust the supply before the Fire Department could respond. Many different groups share responsibility for fixed hydrogen detection systems and alarms. The Industrial Safety Group specifies where alarms are required and which alarms are connected to the Emergency Communications Center. The Industrial Hygiene Group specifies the type and location of detection systems and the maintenance and calibration requirements. Plant Operations Alarm Electricians perform maintenance and calibrations, and Health and Safety Technicians perform periodic visual checks to verify operational readiness.

Training

The most important factor in preventing accidents is a thorough understanding of hydrogen hazards in general and the special hazards of any particular system. Minimum training requirements and emergency shutdown procedures should be specified in the OSP.

Large Hydrogen Systems

Hydrogen systems with a capacity of 3,000 standard cubic feet or more are regulated by OSHA (29 CFR 1910.103, “Hydrogen”) and by various NFPA and Compressed Gas Association

standards. These standards require fire resistant construction, special ventilation, explosion venting, explosion-proof electrical systems (Class I, Group B), and more. Only a few cells in Buildings 232 and 343 can meet these requirements at LLNL. Use of large hydrogen systems elsewhere would require extensive remodeling or new construction.

Liquid Hydrogen

At present there is virtually no use of liquid hydrogen at LLNL; no detailed guidelines are presented here. Contact Hazards Control prior to any use of liquid hydrogen.

Source Documentation

"Hazardous Materials Regulations," Title 49—Transportation, Code of Federal Regulations, Chapter I, Subchapter C, Parts 171-179. Also issued as Bureau of Explosives Tariff No. BOD6000-A; available from Thomas E. Phemister, Agent, Association of American Railroads, 1920 L Street, NW, Washington, DC 20036.

Gas Data Book, available from Matheson Division, Searle Medical Products USA, Inc., Lyndhurst, NJ 07071.

"Hydrogen Usage in the Laboratory," Data Sheet I-700-82, available from National Safety Council, 444 N. Michigan Avenue, Chicago, IL 6061 1 .

D. Peckner and I. M. Bernstein, "Stainless Steel in High Pressure Hydrogen Use," Chapter 46 of *Handbook of Stainless Steels,* 1977. Available from McGraw-Hill Book Co., 1225 Avenue of the Americas, New York, NY 10017.

Code of Federal Regulations Title 29—"Labor," Chapter XVIII, 1910, Section 1910.103, "Hydrogen." U.S.General Services Administration, National Archives and Records Service, Office of Federal Register, Washington, DC. Available from U.S.Government Printing Office, Washington, DC 20402.

Available from the Compressed Gas Association, 500 Fifth Avenue, New York, NY 10036: *Commodity Specification for Hydrogen,* G-5.3; *Compressed Gas Cylinder Valve Outlet and Inlet Connections,* V-l (ANSI B57.1; CSA B96); *Handbook of Compressed Gases Hydrogen,* G-5; *Standard for Gaseous Hydrogen Systems at Consumer Sites,* G-5.1; *Standard for Liquefied Hydrogen at Consumer Sites,* D-5.2.

Available from the National Fire Protection Association, Batterymarch Park, Quincy, MA 02269: *Fire Protection Handbook,* 15th Ed., 1981; *Gaseous Hydrogen Systems at Consumer Sites,* NFPA 50A; *Liquefied Hydrogen System/s at Consumer Sites,* NFPA 50B; *National Electrical Code,* NFPA 70.